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# MONITORING CHEMICAL COMPOSITION OF MEDICAL GLASS USING ATOMIC EMISSION SPECTROSCOPY

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A method is proposed for determining the chemical composition of medcial glass by atom emission spectroscopy with arc excitation. The preparation of samples for measurement does not require acids and alkalis and consists of grinding a glass sample and subsequent dilution in the corresponding buffer solution. The metrological measurement parameters enabled analysis in the prescribed concentration ranges of the main glass elements according to GOST 19808–86.

In view of the growing production volumes in the glass industry and the need for upgrading the quality of finished products, the requirements on monitoring the chemical composition of glass and raw materials for glass production are increasing. As a consequence, more attention is paid to analytical methods using computer-controlled automated instrumental complexes.

The available chemical methods for monitoring glass compositions are labor-consuming and in some cases inaccurate. Errors are frequent in determining small quantities of oxides of chemical components whose content is below 0.5%. The variance in data on the content of certain oxides obtained at different laboratories reaches 900 rel.% [1]. As the determination of silica content takes a long time, this content is often calculated based on the difference [2] summing all errors of determining other components.

The existing atom-absorption method requires additional chemical reactants for dissolving glass, which leads to the distortion of final results, since impurities are introduced via the reactants. Furthermore, some elements form compounds that are hard to dissociate; therefore, it is impossible to fully identify the entire chemical composition in simultaneous analysis.

The multi-element x-ray-fluorescence method that has been proposed lately, despite its advantages in the measuring process, has a number of problems that have a significant impact on final results. As the matrix has a substantial effect on measurement results, this method has a satisfactory error only in a narrow range of concentrations, since the working concentration ranges in glasses are from 62.20 to 73.50% for silicon oxide, i.e., 10% and from 0.70 to 0.96% for potassium oxide, i.e., 0.2%. Rigid requirements are imposed on the state of the surface of the sample, which involves protracted preparation, grinding, and polishing of the sample, requiring additional equipment. Note also the complexity of preparing samples for instrument calibration, which requires a few months' work by qualified analytical chemists [3].

The atomic emission method, which automatically registers spectra on a photodiode scale, is extensively used to determine the elemental composition of different materials. The application of this scale has extended the possibilities of the method and provided for a high accuracy (up to 1 rel.%) in analysis of chemical elements. In contrast to the atom-absorption method, this one allows for simultaneously measuring a large number of elements, whereas the use of arc discharge significantly simplifies the preparation of samples, since no reactants are needed for the decomposition of the matrix. For many elements the smallest measurement range in the atomic emission method is lower than in the x-ray-fluorescence method.

The production of medical glass has to meet the high technical requirements imposed on its chemical composition. The narrow limits of the prescribed chemical compositions of glass call for high-precision methods of analysis that can be ensured by up-to-date measuring instruments.

The purpose of the present study is to develop a fast procedure for analyzing the chemical composition of medical glass using the atomic emission method.

We investigated medical glass NS-3 produced according to GOST 19808–86. The problem included determining the content of the following elements: $SiO_2$, $Al_2O_3$, $B_2O_3$, CaO, MgO, $Na_2O$, $K_2O$, $Fe_2O_3$, and BaO. For this purpose we used a special multichannel atomic-emission instrument AÉMS-03 developed at the Belinteranalit Research-and-Production Company.

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The AÉMS-03 instrument registers spectra on a photodiode scale with subsequent computer processing of data. The software operating in Windows automates the instrument functions and provides a fast data output on spectral line intensities, kinetic curves for exit of elements from the electrode, calibration plots, and the random component of measurement error for each element. The database contains data on more than 50,000 elemental lines and offers wide opportunities for picking up the optimum analytical lines. The output of spectrum processing results is virtually simultaneous with the end of spectrum registration.

The measurement of the elements considered was performed using the standard techniques: the calibration plot method and the additive method using the state standard samples (SSS) of compositions and properties of glasses. The instrument was calibrated based on model samples with a transformed matrix. Samples for instrument calibration were prepared using the SSS of the following solid elements: silicon, aluminum, boron, barium, potassium, calcium, magnesium, and iron. To measure the content of silicon we also used quartz containing 99.99% $SiO_2$ in preparing mixtures.

The preparation of samples for measurements consists in dry grinding of a glass sample to a particle size not more than 0.07 mm.

The conditions for performing measurements were studied, the analytical lines of preset elements given in Table 1 were selected, buffer components were developed, the content of oxides in the considered samples was measured, and statistical data for the metrological certification of the method were accumulated.

The transformation of the matrix of the sample considered due to a buffer component has made it possible to completely eliminate the matrix effect; therefore, measurements could be carried out within wide ranges of element concentrations (Table 1).

The composition of the buffer component is significant for selecting measurement conditions and for the stability of the arc discharge and plasma temperature. For this purpose we modeled and then prepared buffer mixtures containing alkali elements. Furthermore, to stabilize the penetration of chemical elements into the plasma, copper oxide, strontium carbonate, etc. were introduced, which decreased the random component of measurement error and allowed for obtaining reproducible results with a prescribed precision.

To decrease the random component of measurement error, we selected chemical elements that acted as inner reference standards for each oxide considered. The criterion for selecting such elements was their proximity of physicochemical properties and ionization potentials [4]. An appropriate selection of reference standards was assisted by the program option of comparing the kinetic curves of the exit of the analyzed elements from the coal electrode crater into the discharge span with the curves of proposed reference elements. The introduction of a inner standard in the form of a reference element for comparison and the transition to measuring the relative intensity of a spectral line is a powerful instrument for taking into account the effect of random variations in the light source performance or variations in the composition and structure of samples. The performed studies made it possible to decrease the random component of a single error 2 – 5 times. In particular, its decrease is (rel.%): for potassium from 10 to 2, for aluminum from 9 to 3, for calcium from 7 to 1, and for magnesium from 7 to 3.

**TABLE 1**

| Element | Wavelength, nm | Range of determined content, wt.% |
|---|---|---|
| $SiO_2$ | 243.515 | 50.0 – 80.0 |
| $B_2O_3$ | 249.677 | 0.7 – 11.0 |
| $Al_2O_3$ | 237.312 | 0.6 – 10.4 |
| CaO | 315.887 | 0.5 – 8.0 |
| MgO | 333.667 | 0.15 – 2.4 |
| $Na_2O$ | 330.237 | 0.8 – 13.0 |
| $K_2O$ | 404.414 | 0.3 – 5.0 |
| $Fe_2O_3$ | 248.814 | 0.1 – 0.8 |
| BaO | 233.527 | 0.2 – 4.2 |

The results obtained on oxide content in the considered glass NS-3 were used to obtain the indexes of measurement precision (in the form of the mean quadratic deviation) for the following oxides: aluminum) 0.080, barium) 0.080, boron) 0.105, iron) 0.020, potassium) 0.080, calcium) 0.130, silicon) 0.210, magnesium) 0.063, and sodium) 0.105.

The validity of measurements was verified using the SSS of glass compositions and properties certified at the Research Institute of Glass (Gus'-Khrustal'nyi). We obtained the following indexes of validity of measurement for oxides of the following elements: aluminum) 0.020, barium) 0.020, boron) 0.030, iron) 0.005, potassium) 0.020, calcium) 0.030, silicon) 0.050, magnesium) 0.020, and sodium) 0.030.

Statistic data for the metrological certification of the method have been accumulated. For each element analyzed we performed 30 measurements including 2 observations, which in sum totaled a data array of 60 unit measurements. For the method certification we presented 540 reliable values. The following metrological parameters were calculated in certifying the method: the recurrence index – the mean quadratic deviation of recurrence, the reproducibility index – the mean quadratic deviation of reproducibility, and the precision index – the error limits for probability 0.95. The measurement method has been certified at the Ural Research Institute of Metrology. The metrological characteristics are given in Table 2.

Metrological certification of the method confirmed that the method fully meets the requirements imposed on the analysis of glass and glass batches according to GOST 19808–86. The process of measurement and data processing using the AÉMS-03 instrument is fully automated and has a high measurement precision and high speed.

Control measurements of oxides were carried out at different laboratories using the certified method, and their com-

**TABLE 2**

| Element | Index of | | |
|---|---|---|---|
| | recurrence | reproducibility | precision (±) |
| $Al_2O_3$ | 0.080 | 0.100 | 0.20 |
| BaO | 0.080 | 0.100 | 0.20 |
| $B_2O_3$ | 0.105 | 0.125 | 0.25 |
| $Fe_2O_3$ | 0.020 | 0.025 | 0.05 |
| $K_2O$ | 0.080 | 0.100 | 0.20 |
| CaO | 0.130 | 0.150 | 0.30 |
| MgO | 0.063 | 0.075 | 0.15 |
| $SiO_2$ | 0.210 | 0.250 | 0.50 |
| $Na_2O$ | 0.105 | 0.125 | 0.25 |

**TABLE 3**

| Element | Laboratory data, % | | Difference between measurement results, % | Reproducibility limit, % |
|---|---|---|---|---|
| | 1 | 2 | | |
| $SiO_2$ | 73.00 | 72.60 | 0.40 | 0.70 |
| $Al_2O_3$ | 4.46 | 4.57 | 0.11 | 0.28 |
| $B_2O_3$ | 6.04 | 5.95 | 0.09 | 0.35 |
| CaO | 6.03 | 6.04 | 0.01 | 0.42 |
| MgO | 0.94 | 1.01 | 0.07 | 0.21 |
| $Na_2O$ | 8.10 | 8.04 | 0.06 | 0.35 |
| $K_2O$ | 1.70 | 1.68 | 0.02 | 0.28 |
| $Fe_2O_3$ | 0.07 | 0.11 | 0.04 | 0.07 |

pliance with reproducibility limits (admissible variance of measurement results obtained in different laboratories) was verified. The data are given in Table 3.

It can be seen that the differences between the measurement results obtained at different laboratories by different analysts do not exceed the reproducibility limits established in certifying this method at the Ural Research Institute of Metrology. The certified reproducibility limits are fully consistent with the admissible deviations in the production of medical glass specified in GOST 19808–86. Thus, for silicon the admissible deviation is ± 0.5%, i.e. 1%, whereas using the certified method, the deviation is 0.7%; for aluminum it is ± 0.2%, i.e., 0.4%, whereas with the certified method it is 0.28%, etc.

Experimental data obtained by the specified method demonstrate the possibility of fast and high-precision analysis of the chemical composition of glass and glass batches by the atomic emission method using the AÉMS instrument. This enables us to monitor the production process and to significantly improve the quality of the product.

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